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Effects of Crucible Wetting During Solidification of Immiscible Pb–Zn

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EFFECTS OF CRUCIBLE WETTING DURING SOLIDIFICATION OF IMMISCIBLE Pb-Zn ALLOYS

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Abstract

Many industrial uses for liquid phase miscibility gap alloys have been proposed. However, the commercial production of these alloys into useful ingots with a reasonable amount of homogeneity is arduous because of their immiscibility in the liquid state. In the low-g environment of space gravitational settling forces are abated, thus solidification of an immiscible alloy with a uniform distribution of phases becomes feasible. Elimination of gravitational settling and coalescence processes in low-g also makes possible the study of other separation and coarsening mechanisms.

Even with gravitational separation forces reduced, many low-g experiments have resulted in severely segregated structures. The segregation in many of these cases was due to preferential wetting of the crucible by one of the immiscible liquids. Our objective was to analyze the wetting behavior of Pb-Zn alloys on various crucible materials in an effort to identify a crucible in which the fluid flow induced by preferential wetting is minimized. It is proposed that by choosing the crucible for a particular alloy so that the difference in surface energy between the solid and two liquid phases is minimized, the effects of preferential wetting can be diminished and possibly avoided.

Qualitative experiments were conducted and have shown the competitive wetting behavior of the immiscible Pb-Zn system and 13 different crucible materials. The three crucibles preferentially wet by Zn were attacked by the molten Zn and partially or completely dissolved. Of these Nb reacted the least. Of the crucible materials preferentially wet by Pb, carbon and tungsten had the largest dihedral angles, thus C and W are believed to have the smallest surface energy difference and therefore minimize the possibility of complete wetting and associated fluid flows. It is expected that this procedure will assist in the choice of crucibles, for other alloys as well as Pb-Zn, which will reduce the fluid flow and segregation normally caused by competitive wetting in low-g.

Introduction

An alloy containing a liquid-phase miscibility gap has a two-phase field consisting of immiscible liquids. The Pb-Zn system has such a liquid-phase miscibility gap as shown in the phase diagram in Fig. 1.[1,2] Hundreds of immiscible alloys exist.[2] However, the processing of these alloys is generally considered impractical due to their immiscibility in the liquid state. In the immiscible field the two liquids separate due to their different densities, similar to the way oil and water separate.

The low-g environment of space provides a unique opportunity to process these alloys. In low-g it is possible the immiscible liquid droplets which form in the parent liquid will not segregate since gravitational Stokes settling forces have been nearly eliminated. The ability to study this large group of alloys without gravity-induced segregation has sparked new interest in these alloys and their possible applications. Liquid-phase miscibility gap alloys are presently being developed for electrical contact applications. Other possible uses are as superconductors, catalysts, permanent magnets, bearings and superplastic materials.[4,5] To develop immiscible alloys for these applications ingots are needed with a uniform distribution of phases. Solidification of these alloys in low-g will help us to attain this goal and contribute to our understanding of the processes by which immiscible alloys segregate on earth.

This research was done in support of the design and development of a planned Space Shuttle experiment using a Get-Away-Special canister.[6,7]

Many of the immiscible alloys previously processed in low-g have resulted in severely segregated structures due to unexpected fluid flow and other uncertain experimental parameters.[8-12] These experiments have shown the importance of the wetting behavior of the two immiscible liquids and the crucible. Upon cooling into the immiscible phase field small droplets of at least one of the two liquids form. The two liquids have different compositions and a different equilibrium wetting angle with the crucible. Consider, for example, a Pb-rich droplet in a melt of average composition Zn-40 wt % Pb, just touching the alumina crucible containing the melt. If the Pb-rich alloy preferentially wets the alumina relative to the parent liquid the Pb-rich droplet will tend to spread out on the crucible. This motion will cause fluid flow, thus helping other Pb-rich droplets to contact the crucible. This autocatalytic process promotes further coalescence and segregation of the two liquids. In low-g this may result in the Pb-rich liquid coating the inside of the crucible and the Zn-rich liquid collecting in the center. Thus nearly complete segregation of the two phases may result even though gravity-driven sedimentation has been eliminated.

Macrosegregation due to preferential wetting of this type may be avoided in less concentrated alloys ($\approx$10 vol % or less) by the majority phase preferentially wetting the crucible.[13,14] This of course does not help us when attempting to process more concentrated alloys. Also, there is evidence that minority phase droplets which do not wet the crucible may be pushed away from the crucible wall causing flow and macrosegregation.[14] Thus, a knowledge of the wetting behavior is required for the interpretation of structures and the efficient design of crucibles for low-g experimentation.

Cahn's theory states that complete preferential wetting of the crucible by one of the liquids occurs at temperatures near the critical point at the top of the immiscible dome.[15,16] The balance of interfacial energies between the two liquids and the crucible is given by

$$\gamma_{L_1L_2} \cos\theta = \gamma_{SL_1} - \gamma_{SL_2} , \qquad (1)$$

where the angle θ this the dihedral angle shown in Fig. 2, $\gamma_{L_1L_2}$ is the interfacial free energy at the boundary between the two immiscible liquids, and γ_{SL_1} and γ_{SL_2} are the solid-L_1 and solid-L_2 interfacial free energies respectively. Complete wetting occurs when θ equals zero and at undefined values of $\cos\theta$ such that

$$\gamma_{L_1L_2} < |\gamma_{SL_1} - \gamma_{SL_2}| . \qquad (2)$$

Heady and Cahn[16] showed in the methylcyclohex ane-perfluoromethyl-cyclohexane immiscible system that the left-hand side of Eq. (2) decreases to zero with a $\Delta T_{UC}^{1.3}$ relationship and the right-hand side as $\Delta T_{UC}^{0.3}$, where ΔT_{UC} is the undercooling, or temperature difference below the immiscible dome. Thus, at some temperature below the critical temperature perfect wetting of any solid by one of the liquid phases is expected. By choosing the crucible for a particular alloy so that the difference in surface energy between the solid and two liquid phases is minimized, the effects of preferential wetting may be diminished and possibly avoided.

Many theories have been developed in an effort to model and predict solidification and the final structure of immiscible alloys.[12,17] Attempts have been made to study and model separation and coarsening mechanisms.[15,18] These mechanisms are often overshadowed by the effects of preferential wetting, thus making their study difficult if not impossible. Elimination of crucible wetting processes would enable us to study these mechanisms as well as help in the production of a less segregated product in low-g. The objective of the present work was to identify a crucible material in which the fluid flow induced by the wetting behavior between the Pb-Zn alloy and crucible would be eliminated or significantly reduced.

A series of experiments was conducted and has qualitatively shown the competitive wetting characteristics between the Pb-Zn immiscible alloy system and various crucible materials. Approximate wetting angles at the crucible-Pb-Zn interface were measured in an effort to find a crucible such that the interfacial energies between the crucible and liquids is minimized. It is hoped that this analysis will assist in the choice of crucibles, for other alloys as well as Pb-Zn, which will reduce the fluid flow and segregation normally caused by competitive wetting in low-g.

Experimental Procedure

The crucible materials listed in Table 1 were cut to fit inside 5/8 in. i.d. fused silica test tubes and placed vertically in the tube with approximately 25 g of Pb-35 wt % Zn (when solid approximately Pb-46 vol % Zn). The Pb and Zn material used was 99.999 percent pure. The crucible material and alloy were sealed in a fused silica tube or a stainless steel container. In some cases, as noted in Table 1, crucibles were made of the test material. In these cases wetting angles were measured from the container crucible itself. Figure 3 shows schematically the test tube and crucible test material arrangement. All samples were heated above 816 °C, briefly removed from the furnace and mixed by gentle agitation, reheated to above 816 °C, soaked at temperature for at least 10 min and slowly cooled. The average cooling rate through the immiscible liquid region and solidification was 0.2 °C/sec.

After solidification, ingots were sectioned longitudinally along the centerline, perpendicular to the crucible test material, and mounted in metallographic epoxy such that the cross section could be viewed. Micrographs were taken after polishing and approximate wetting angles measured from the micrographs. The wetting angles listed in the table are meant only as a qualitative comparison of wetting behavior of the different crucible materials. The wetting angle θ was always measured through the preferential wetting liquid as shown in Fig. 2.

Results

Table 1 shows the crucible material tested, preferential wetting liquid phase, and approximate wetting angle. The material Macor is a fully dense machinable glass supplied by Corning Glass. The ZYP coating was used on a stainless steel container and is a silica-based paintable coating designed for metal substrates and supplied by ZYP Coatings Inc. The SiC was a hot-isostatically-pressed rectangular bar. The wetting angles in Table 1 are the mean of several measurements. Three to ten measurements were made to determine θ. The higher number of samples were made of materials in which large scatter appeared in θ. Figures 4(a) to (c) show Pb-Zn wetting behavior upon Nb, SiC, and W respectively.

All of the materials preferentially wet by Zn were attacked by the Zn and reacted with it. Niobium reacted the least and nickel the most. Nickel completely dissolved in the molten zinc. The reaction with niobium was slightly less severe than that with cobalt. Zinc completely wet the cobalt plate and reacted to form Co-Zn intermetallics at the Co plate-Zn interface. Such potential reactions must be considered when choosing crucible materials. If Zn wetting is required and contamination of the Zn can be tolerated, Nb is the recommended crucible material.

Of the crucible materials which were preferentially wet by Pb, carbon and tungsten had the two largest three phase dihedral angles, θ. Therefore C and W are the best choice of the crucible materials tested here when preferential wetting by Pb over Zn and a minimization of $\gamma_{SL_1}-\gamma_{SL_2}$ is desired.

Summary

In order to minimize the fluid flow and segregation caused by preferential wetting of one of the immiscible liquid phases in low-g, the majority phase should preferentially wet the container and the surface energy difference, $\gamma_{SL_1}-\gamma_{SL_2}$, minimized. Smaller surface energy differences are characterized by larger values of the dihedral angle, Θ.

Thirteen readily available materials were investigated as possible container materials for Pb-Zn alloys. The phase which preferentially wet each test material was determined and approximate contact wetting angles measured.

The three crucible materials preferentially wet by Zn were also chemically attacked by the Zn. Niobium was the least reactive and is the recommended material for use when preferential wetting by Zn is required and Nb contamination of the Zn can be tolerated.

Of the crucible materials preferentially wet by Pb, C and W had the two largest dihedral angles and thus are the recommended materials when wetting by Pb over Zn is required and minimization of fluid flow due to critical and preferential wetting is desired.

References

1. Hansen, M., Constitution of Binary Alloys, McGraw-Hill, 1959.

2. Ang, C.Y. and Lacy, L.L., "Apollo-Soyuz Test Project, Preliminary Science Report," NASA TM X-58173, 1976.

3. Reger, J.L., "Study of Processing Immiscible Materials in Zero Gravity," TRW-14725-6010-RU-00, TRW Systems Group, Redondo Beach, CA, May 1973, NASA CR-120222.

4. Markworth, A.J., Oldfield W., Duga, J., and Gelles, S.H., "Investigation of Immiscible Systems and Potential Applications," NASA CR-120667, 1975.

5. Reger, J.L. and Yates, I.C. Jr., "Preparation and Metallurgical Properties of Low Gravity Processed Immiscible Materials," AIAA Paper 74-207, Jan. 1974.

6. Turner, G.D., de Groh, H.C. III, and Antoon, F.A., "Low-Cost Get-Away-special (GAS) Furnace," Materials Processing in the Reduced Gravity Environment of Space, MRS Symp. Proc. Vol. 87, R. H. Doremus and P.C. Nordine, eds., Materials Research Society, Pittsburgh, PA, 1987, pp. 305-312.

7. Turner, G.D., Probst, H.B., and de Groh, H.C. III,, "Surface Energy Effects in the Solidification of Immissible Fluids Under Microgravity," J.G. Morse, ed., The Metallurgical Society, Warrendale, PA, 1987, pp. 89-90.

8. Gelles, S.H., Giessen, B.C., Glicksman, M.E., Margrave, J.L., Markovitz, H., Nowick, A.S., Verhoeven, J.D., and Witt, A.F., "Materials Science Experiments in Space," NASA CR-2842, 1978.

9. Materials Processing in Space: Early Experiments, NASA SP-443, R.J. Naumann and H.W. Herring, eds., NASA, Washington, DC, 1980, p. 92.

10. Ahlborn, H. and Loehberg, K., "Aluminum-Indium Experiment SOLUOG - A Souding Rocket Experiment on Immiscible Alloys," AIAA Paper 79-0172, Jan. 1979.

11. Potard, C., "Directional Solidification of Al-In Alloys at Microgravity-Results of Basic Preparatory Investigations," AIAA Paper 79-0173, Jan. 1979.

12. Gelles, S.H. and Markworth, A.J., "Microgravity Studies in the Liquid-Phase Immiscible System: Aluminum-Indium," AIAA Journal, Vol. 16, No. 5, May 1978, pp. 431-438.

13. Frazier D.O., Facemire, B.R., Kaukler, W.F., Witherow, W.K., and Fanning, U.," Separation Process During Binary Monotectic Alloy Production," NASA TM-82579, 1984.

14. Potard, C., "Structures of Immiscible Al-In Alloys Solidified Under Microgravity Conditions," IAF Paper 81-140, Sept. 1981.

15. Cahn, J.W., "Critical Point Wetting," Journal of Chemical Physics, Vol. 66, No. 8, Apr. 15, 1977, pp. 3667-3672.

16. Heady, R.B. and Cahn, J.W., "Experimental Test of classical Nucleation Theory in a Liquid-Liquid Miscibility Gap System," Journal of Chemical Physics, Vol. 58, No. 3, Feb. 1973, pp. 896-910.

17. Walter, H.U., ed., Fluid Sciences and Materials Science in Space, Springer-Verlag, New York, 1987, p. 517.

18. Young, N.O., Goldstein, J.S., and Block, M.J., "The Motion of Bubbles in a Vertical Temperature Gradient," Journal of Fluid Mechanics, Vol. 6, Pt. 3, Oct. 1959, pp. 350-356.

TABLE 1. - PREFERENTIAL WETTING LIQUID AND QUALITATIVE WETTING ANGLES BETWEEN Pb-Zn IMMISCIBLE LIQUIS ON VARIOUS CRUCIBLE MATERIALS

Crucible material	Form of crucible material	Preferential wetting liquid	Postsolidification wetting angle, θ, deg
Niobium	Sheet	Zn	0
Cobalt	Plate	Zn	0
Nickel	Plate	Zn	---
SiC	HIPed bar	Pb	8
Macor glass	Crucible	↓	9
Fused silica	Crucible	↓	11
Al_2O_3	HIPed bar	↓	11
ZYP coating "S-prime-mod"	Crucible	↓	13
Boron nitride	Plate	↓	14
Molybdenum	Sheet	↓	24
Tantallum	Sheet	↓	27
Tungsten	Sheet	↓	37
Carbon	Plate	↓	48

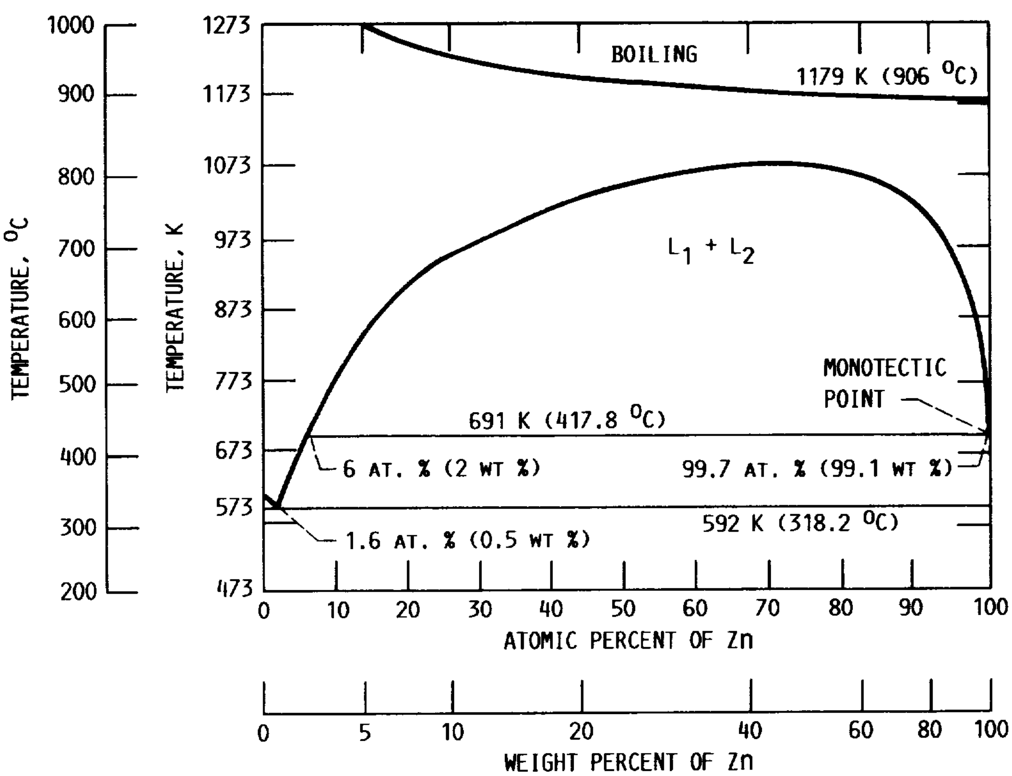


FIGURE 1. - PHASE DIAGRAM FOR Pb-Zn [1,2].

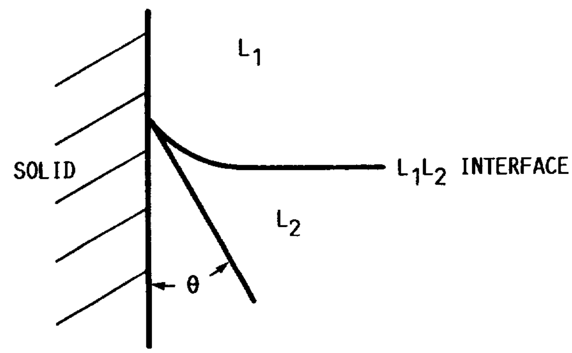


FIGURE 2. - THETA (θ) IS THE DIHEDRAL ANGLE AT THE THREE PHASE JUNCTION MEASURED THROUGH THE PREFERENTIAL WETTING LIQUID.

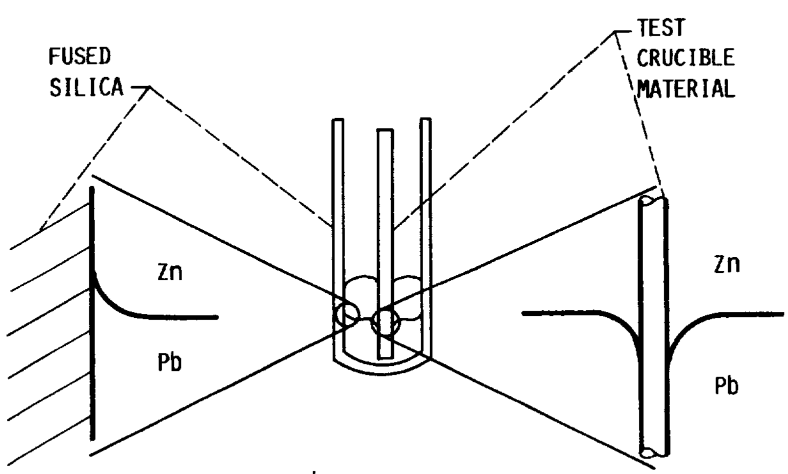
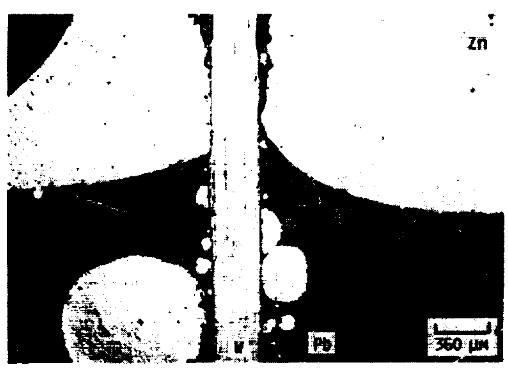


FIGURE 3. - SCHEMATIC CROSS SECTION OF SILICA TEST TUBE, Pb-Zn INGOT, AND TEST CRUCIBLE MATERIAL. (LEFT, WETTING AT CONTAINER CRUCIBLE WALL; RIGHT, WETTING AT TEST CRUCIBLE MATERIAL.)

(a) Nb SHEET. ZINC COMPLETELY WETS THE Nb.

(b) SiC HIPED BAR.



(c) W SHEET.

FIGURE 4. - OPTICAL PHOTOMICROGRAPH OF Pb-Zn INGOTS WITH VARIOUS CRUCIBLE TEST MATERIALS PLACED DOWN THE CENTER PRIOR TO MELTING.

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16. Abstract

Many industrial uses for liquid phase miscibility gap alloys have been proposed. However, the commercial production of these alloys into useful ingots with a reasonable amount of homogeneity is arduous because of their immiscibility in the liquid state. In the low-g environment of space gravitational settling forces are abated, thus solidification of an immiscible alloy with a uniform distribution of phases becomes feasible. Elimination of gravitational settling and coalescence processes in low-g also makes possible the study of other separation and coarsening mechanisms. Even with gravitational separation forces reduced, many low-g experiments have resulted in severely segregated structures. The segregation in many of these cases was due to preferential wetting of the crucible by one of the immiscible liquids. Our objective was to analyze the wetting behavior of Pb-Zn alloys on various crucible materials in an effort to identify a crucible in which the fluid flow induced by preferential wetting is minimized. It is proposed that by choosing the crucible for a particular alloy so that the difference in surface energy between the solid and two liquid phases is minimized, the effects of preferential wetting can be diminished and possibly avoided. Qualitative experiments were conducted and have shown the competitive wetting behavior of the immiscible Pb-Zn system and 13 different crucible materials. The three crucibles preferentially wet by Zn were attacked by the molten Zn and partially or completely dissolved. Of these Nb reacted the least. Of the crucible materials preferentially wet by Pb, carbon and tungsten had the largest dihedral angles, thus C and W are believed to have the smallest surface energy difference and therefore minimize the possibility of complete wetting and associated fluid flows. It is expected that this procedure will assist in the choice of crucibles, for other alloys as well as Pb-Zn, which will reduce the fluid flow and segregation normally caused by competitive wetting in low-g.

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